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# Space Vehicle Material and Plume Interactions with the Low Earth Orbital Environment

## **Final Technical Performance Report**

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## OBJECTIVES

### Proposed Objectives

The general goals of the proposed work were to provide vital experimental data for improved modeling of rocket plume signatures and to evaluate and guide the design of new inorganic/organic POSS-containing nanocomposite materials which could be space-durable alternatives to polymers that are currently employed on spacecraft. Proposed experiments were focused on 6 areas: (1) crossed-beams reactive scattering dynamics of  $O(^3P)$  + plume exhaust species, with identification of reactive channels and branching ratios, as well as determination of excitation functions and differential cross sections; (2) erosion yields and rates of POSS-containing polymers under hyperthermal O-atom bombardment; (3) *ex situ* chemical and topographical analyses of exposed POSS-polymer surfaces; (4) *in situ*, real-time measurements of chemical changes of POSS-polymer surfaces under O-atom bombardment, studied by reflectance absorption FTIR spectroscopy; (5) investigation of scattering dynamics of O-atom interactions with POSS-polymer surfaces via beam-surface scattering; (6) concomitant exposures of POSS-polymers with atomic oxygen and VUV light (both for exposure experiments and beam-surface scattering experiments).

### Proposal Abstract

A successful missile defense capability depends critically on the ability to analyze and model spacecraft or missile rocket plume signatures at low-Earth orbital altitudes. An important component of plume signatures is chemiluminescent emission from internally excited molecules that are formed when molecules in a rocket exhaust stream collide with atmospheric species (mainly atomic oxygen) at very high relative velocities. These interactions have been difficult, if not impossible, to study in the laboratory. Recent advances in the use of molecular beam techniques to study hyperthermal atomic and molecular collisions provide the capability to understand details of plume chemistry. Concomitant advances in theoretical approaches that use state-of-the-art quantum mechanical and molecular collision methods now make it possible to model plume signatures. With experimental validation, the theoretical techniques may be used to provide accurate signature modeling that will be critical to a missile defense system.

Atomic oxygen not only reacts with rocket exhaust streams, but it also inhibits the durability of space vehicles. The high relative velocity between a spacecraft and ambient O atoms results in an O-atom reactivity that may be more than 100 times thermal. Oxygen atoms may act alone or in combination with micrometeoroids and debris, vacuum ultraviolet light, and charged particles to degrade materials. The same hyperthermal molecular beam techniques that may be used to extend our knowledge of plume chemistry are now being employed to study spacecraft materials degradation in low-Earth orbit. The new addition of theoretical calculations to the study of space environmental effects has enhanced the overall effort dramatically. Through continuing efforts to increase basic understanding of degradation mechanisms, new test protocols, mitigation schemes, and materials have been and are being developed. A paradigm shift in durable materials design has occurred very recently. Hybrid inorganic/organic materials may be able to serve as drop-in replacements for current polymers that degrade in space. New experiments have shown that a class of materials based on copolymerization of polyhedral oligomeric silsesquioxane (POSS) nanoparticles with various existing organic polymers may produce polymer nanocomposites that can survive in the harsh low-Earth orbital environment. An evolving fundamental understanding of how to predict and mitigate materials degradation in



the low-Earth orbital environment is clearly driving progress toward the goal of producing more durable spacecraft.

Experimental studies of hyperthermal O-atom reactions with gaseous species and with surfaces, relevant to plumes and materials degradation, respectively, will be conducted in the PI's laboratory, and theoretical support will come from collaborators at Northwestern University and Spectral Sciences, Inc. New POSS-containing materials will be developed and supplied by the POSS Polymer Group at the Air Force Research Laboratory at Edwards AFB. The PI will maintain close contact with researchers at several Air Force Labs (Hanscom, Wright Patterson, Edwards, and Aerospace Corp.) in order to ensure that the research effort will stay relevant to Air Force and DoD interests. The experimental work will capitalize on the research infrastructure already in existence in the PI's lab, while also extending this infrastructure with the use of a new apparatus that has only just been set up. The existing apparatus will be used for crossed-beams and beam-surface studies of reaction dynamics, and the new apparatus will be used to elucidate the surface chemistry of atomic-oxygen-exposed surfaces through *in situ* measurements by Fourier transform infrared spectroscopy.

The proposed project has direct relevance to critical Air Force issues involving spacecraft survivability and situational awareness. All those involved at Montana State University will work closely with Air Force personnel to provide support to Air Force missions with fundamental research that can be uniquely done in the PI's laboratory.

## SUMMARY OF EFFORT

The setup of a UHV apparatus with a hyperthermal O-atom source was completed, and this apparatus is available as infrastructure for *in-situ* investigations of surfaces modified by hyperthermal atomic-oxygen. The laser-breakdown, hyperthermal atomic-oxygen source has been dramatically improved by the redesigned molecular beam valve. A quartz crystal microbalance has been used to study the erosion kinetics of a number of POSS-containing and  $\text{Al}_2\text{O}_3$ -coated polyimides during exposure to hyperthermal O atoms. Crossed-beams experiments in the PI's lab and corresponding theoretical studies by collaborators have revealed the dynamics of  $\text{O}(^3P)$  reactions with several small molecules that might be found in rocket exhaust gases. Beam-surface scattering experiments, in which hyperthermal O and Ar atoms were directed at fluoropolymer surfaces (with and without the presence of VUV light), found synergistic effects involving O-atom reactions, VUV light, and collision-induced dissociation that may dominate the mechanism of Teflon degradation in low Earth orbit. The dynamics of hyperthermal Ar scattering from graphite showed the risk of using simple models to interpret hyperthermal gas-surface interactions. The exposure of numerous samples to a beam of hyperthermal oxygen atoms confirmed the O-atom resistance of several new POSS polymers and deepened our understanding of the erosion mechanisms of polymers. The infrastructure to study hyperthermal interactions has been transitioned to a Center for Laboratory Studies of Rocket Plume Chemistry and to the support of two STTR projects aimed at the development of improved coatings for use in space.



## **ACCOMPLISHMENTS/NEW FINDINGS**

### **Pulsed molecular beam valve and the hyperthermal O-atom source**

A major endeavor of the project became the redesign of the piezoelectric pulsed valve for the hyperthermal O-atom beam source. This valve was the chronic weak link in the stable and reliable operation of the source. We had been using a valve based largely on the “Proch and Trickl” valve, which was described in a Review of Scientific Instruments publication in the 1980s. This valve uses a piezoelectric crystal (PZT) disk bonded to a stainless steel disk as an actuator to pull an O-ring away from the nozzle orifice. We found that the actuator, which was purchased commercially, barely provided enough force to open the valve when high backing pressures ( $>15$  bar) were used. However, better performance could be obtained when pressures of 30-40 bar were used. We therefore designed and learned how to fabricate our own actuators, which use two PZT crystals instead of one. With the old valve design, the PZT crystal easily developed severe cracks during operation, which led to degradation of performance and often failure of the valve during a one- or two-day experiment. The new actuators are able to operate for months with no degradation of performance. In addition to the actuator, we have made huge strides in how to mount, align, and adjust the O-ring seal in the valve, which has also contributed to improved valve performance: more gas produced and more stable operation. We have also discovered a hysteresis in the PZT crystals, which was leading to a change in tension on the O-ring during operation. We figured out how to deal with this hysteresis by incorporating the capability to externally adjust the O-ring tension in our redesign of the valve. Besides the key points mentioned here, we learned a huge amount about the subtle details of the valve parameters and how they affect the performance of our hyperthermal O-atom source. At this time, we are routinely using our new valve, and we have made a complete set of drawings that were used to duplicate the valve. With the new valve, the O-atom intensity in our experiments is now about twice what it was with the old valve, and our “down-time” due to valve problems is now almost negligible. The new valve design is available for sharing, and we have provided the design to Prof. Steven Sibener of the University of Chicago for use with his hyperthermal O-atom source.

### **UHV apparatus for O-atom exposures and *in situ* surface analysis**

During the initial stages of the project, a new O-atom source was added to a UHV surface science apparatus that was acquired with funds from the previous DEPSCoR grant. The new source required the design and fabrication of several pieces of custom vacuum hardware and O-atom source components. (A second pulsed valve, as described above was completed and designated for this apparatus.) In addition, many commercial vacuum pumps, gauges, and gate valves were added to the apparatus in conjunction with the new source. And finally, a new CO<sub>2</sub> laser was purchased, which was needed because the O-atom source is a “laser-detonation” source. Besides the new source, we added a mass spectrometric capability to the apparatus, because successful operation of the hyperthermal source requires almost constant interrogation of the beam that is produced. Associated with the mass spectrometer was some custom vacuum equipment to allow for differential pumping. The intention of this apparatus was to provide added capability to support studies of O-atom interactions with POSS polyimide materials for the



project, and it also represented added infrastructure for future experiments and testing relevant to space environmental effects.

Although the apparatus was set up, it was ultimately not used for the project, and funds and some of the new equipment were applied instead to experiments on the already existing crossed-beams apparatus. The redesign of the pulsed valve and necessary testing required much more time and expense than expected. In addition, the crossed-beams experiments posed a considerable challenge, both in the collection of the data and in the analysis, and these experiments received a great deal of focus. Finally, an originally unanticipated experiment that used a quartz crystal microbalance to investigate the efficacy of atomic layer deposition coatings was undertaken after discussions with the program manager. This experiment proved fruitful but was one of the factors that caused the experiments on the UHV apparatus to be abandoned. Even though these experiments were abandoned, the project was successful on many fronts, generating new knowledge of many hyperthermal gas-phase and gas-surface reactions/interactions and revealing much about the durability of various materials that are exposed to hyperthermal oxygen atoms.

### Cross-beams studies of gas-phase reaction dynamics at hyperthermal collision energies

#### $O(^3P) + D_2$

A crossed-beams study of the  $O + D_2$  reaction was carried out in the PI's lab, and the results were compared with theoretical calculations performed by Prof. George Schatz of Northwestern University. A paper was published on the combined experimental and theoretical studies of the dynamics, with emphasis on a center-of-mass (c.m.) collision energy of 25 kcal mol<sup>-1</sup>. The experiments were conducted with a crossed molecular beams apparatus, employing a laser detonation source to produce hyperthermal atomic oxygen and mass spectrometric detection to measure the product angular and time-of-flight distributions. The novel beam source, which enabled these experiments to be conducted, contributed unique challenges to the experiments and to the analysis, so the experimental methods and approach to the analysis were discussed in much detail. Three different levels of theory were used: (1) quasiclassical trajectories (QCT), (2) time independent quantum scattering calculations based on high quality potential surfaces for the two lower-energy triplet states, and (3) trajectory-surface-hopping (TSH) studies that couple the triplet surfaces with the lowest singlet surface using a spin-orbit Hamiltonian derived from *ab initio* calculations. The latter calculations explored the importance of intersystem crossing in the dynamics. Both experiment and theory showed that inelastically scattered O atoms scatter almost exclusively in the forward direction, with little or no loss of translational energy. For the reaction,  $O(^3P) + D_2 \rightarrow OD + D$ , the experiment showed that, on average, ~50% of the available energy went into product translation and that the OD product angular distributions were largely backward-peaked. These results may be interpreted in light of the QCT and TSH calculations, leading to the conclusion that the reaction occurs mainly on triplet potential energy surfaces, with at most minor intersystem crossing to a singlet surface. Reaction on either of the two low-lying reactive triplet surfaces proceeds through a rebound mechanism in which the angular distributions are backward-peaked and the product OD is both vibrationally and rotationally excited. The quantum scattering results were in good agreement with QCT calculations, indicating that quantum effects are relatively small for this reaction at a collision energy of 25 kcal mol<sup>-1</sup>.



### $O(^3P) + H_2O$

The  $O(^3P) + H_2O \rightarrow HO_2 + H$  reaction excitation function was measured in a crossed-beams experiment that employed a source of hyperthermal  $O(^3P)$  atoms, and the experimental findings were augmented by direct dynamics calculations (performed in the lab of Prof. George Schatz of Northwestern University). The experimental barrier was found to be  $60 \pm 2 \text{ kcal mol}^{-1}$ , and the shape of the experimental excitation function in the threshold region matched the excitation function calculated at the B3LYP/6-31G(d,p) level of theory for reaction on the lowest triplet potential energy surface. Direct dynamics calculations on this surface showed that the excitation function for production of  $HO_2$  rises from threshold to a maximum near  $115 \text{ kcal mol}^{-1}$  and then decreases when  $HO_2$  can be formed with sufficient internal energy to dissociate. At collision energies up to  $\sim 115 \text{ kcal mol}^{-1}$ , an  $S_N2$ -like mechanism dominates, and  $HO_2$  scatters mainly in the backward direction with respect to the initial direction of the reagent O atoms. When the collision energy is greater than  $\sim 115 \text{ kcal mol}^{-1}$ , the only trajectories that lead to stable  $HO_2$  are those in which an H atom is oriented toward the incoming reagent O atom, in which case the  $HO_2$  scatters in the sideways and forward directions. Therefore, the scattering dynamics of  $HO_2$  exhibit a marked dependence on the collision energy, arising from a qualitative change in the reaction mechanism as the energy increases from near-threshold ( $\sim 60 \text{ kcal mol}^{-1}$ ) to greater than  $\sim 115 \text{ kcal mol}^{-1}$ .

### $O(^3P) + CO$

Crossed-molecular beams methods (PI's lab) and theoretical calculations (conducted by Dr. Matt Braunstein of Spectral Sciences, Inc.) have been used to investigate the hyperthermal interactions of  $O(^3P)$  with CO at c.m. collision energies near  $83 \text{ kcal mol}^{-1}$  (corresponding to a relative velocity near  $8 \text{ km s}^{-1}$ ). Inelastic scattering experiments on the process,  $^{16}O(^3P) + C^{18}O(v,j) \rightarrow C^{18}O(v',j') + ^{16}O$ , indicate that oxygen atoms mainly scatter from  $C^{18}O$  with relatively large impact parameters and lead to forward scattering with little change in direction and translational energy. Averaged over all inelastic collisions,  $\sim 15$  percent of the collision energy is transferred to internal energy in CO. Although this fraction is relatively small, the collision energy is high, so internal excitation of CO above an energy corresponding to  $v=1$  still occurs in approximately 84 percent of all inelastic collisions. The reactive channel,  $^{16}O(^3P) + C^{18}O \rightarrow ^{16}OC + ^{18}O$ , created  $^{16}OC$  products that are scattered mainly in the forward direction, while a minority of collisions lead to  $^{16}OC$  scattered in the sideways and backward directions. The  $^{16}OC$  product formed in the reactive channel had a very broad translational energy distribution, with  $\sim 40$  percent, on average, of the available (collision) energy transferred into internal excitation. Approximately 97 percent of reactive collisions produce  $^{16}OC$  with internal energies greater than an energy corresponding to  $v=1$ , and about 8 percent of collisions lead to internal energies greater than  $v=11$ . Quasiclassical trajectory calculations on computed triplet potential energy surfaces are in excellent agreement with the experimental results. The calculations reveal a mechanism for large energy transfers, into both rotation and vibration, where the reagent O atom encounters the carbon end of the CO molecule with a range of impact parameters in a bent O-C-O geometry ( $\sim 80^\circ$ – $140^\circ$ ). The three atoms linger together for less than a rotational period but usually for more than a CO vibrational period, and the transient complex breaks up into either inelastic or reactive products. The inelastic trajectories that lead to significant energy transfer to the CO may thus be considered failed reactive collisions. The similarity in inelastic and reactive trajectories that lead to high vibrational excitation in the CO



product is supported by calculated translational energy and angular distributions for reactive and inelastic collisions without the CO( $v=0$ ) product. These distributions, which remove contributions from purely inelastic rotational excitation, are nearly identical.

The theoretical calculations, which use a modest one-electron basis set and level of theory, have been used to predict inelastic and reactive cross sections at a variety of collision energies and to predict infrared emission spectra that compare favorably with earlier measurements. Given the accuracy with which the calculations predict the collision dynamics observed in our high-fidelity crossed-beams experiments, we expect the mechanistic insights and additional predictions offered by the theory to be accurate, too.

It is surprising that the predictions from the present level of theory match all the details of the various experimental results so well. However, at these high collision energies, the present level of theory appears to describe the important parts of the potential adequately. The QCT approach works well because quantum effects are small, and higher levels of theory will not change the good agreement between measurements and the present modeling results. Such a picture of hyperthermal chemistry would be consistent with several recent experimental/modeling studies where surprisingly good agreement between a modest level of theory and experiment was seen. It could also be the case that several unrelated modeling errors are favorably canceling out for this particular chemical system at these energies, that the good agreement is accidental, and that use of higher levels of theory will yield worse comparisons with measurements. The O + CO system is small enough that much higher levels of theory can be applied to obtain new potentials, and that quantum scattering approaches could perhaps be applied even at these high energies with present modeling algorithms and computer hardware. Such studies for this experimentally well-characterized system would be valuable to gauge the level of theory needed to describe hyperthermal chemistry in general.

### O( $^3P$ ) + HCl

The hyperthermal reaction of O( $^3P$ ) with HCl or DCl was investigated with crossed-molecular beams methods at c.m. collision energies from 45 – 108 kcal mol<sup>-1</sup>. The experimental findings were augmented by direct dynamic calculations at c.m. collision energies from 45 – 207 kcal mol<sup>-1</sup>. The direct dynamics calculations were carried out in the lab of Prof. George Schatz of Northwestern University. The reaction may proceed through two primary pathways: (1) O + HCl → OH + Cl (H-atom abstraction) and (2) O + HCl → ClO + H (H-atom elimination). The H-atom abstraction reaction proceeds through a stripping mechanism, with large impact parameters, where the OH products predominantly scatter in the forward direction with little change in direction and energy with respect to those of the initial reagent O atoms. The H-atom elimination reaction undergoes collisions with small impact parameters. The dynamics of the ClO product strongly depend on collision energy and are consistent with the excitation function. The shape of the experimental excitation function matched the excitation function calculated at the B3LYP/6-31G(d,p) level of theory. Direct dynamics calculations showed that the excitation function for production of ClO rises from threshold to a maximum near 115 kcal mol<sup>-1</sup> and then decreases when ClO can be formed with sufficient internal energy to dissociate. At collision energies up to ~115 kcal mol<sup>-1</sup>, an S<sub>N</sub>2-like mechanism dominates, and ClO scatters mainly in the backward direction with respect to the initial direction of the reagent O atom. When the collision energy is greater than ~115 kcal mol<sup>-1</sup>, the only trajectories that lead to stable ClO are those in which an H atom is oriented toward the incoming reagent O atom, in which case the ClO scatters in the sideways and forward directions. This collision-



energy dependent scattering dynamics can be considered general for hyperthermal H-atom elimination reactions with heavy + heavy-light mass combinations.

#### $O(^3P) + C_2H_6$

The dynamics of the reaction of hyperthermal  $O(^3P)$  with ethane were studied in detail and two reaction pathways were observed for the first time. Experiments were performed in the PI's lab, and theoretical calculations were conducted by George Schatz (Northwestern University). Four channels were studied: inelastic scattering, H-atom abstraction, H-atom elimination, and C–C bond breakage. Inelastically scattered O-atoms were found to be mostly forward-scattered at large impact parameters with very little loss of translational energy. Less probable, smaller impact parameter, non-reactive collisions resulting in large losses in translational energy were also observed at more sideways and backwards c.m. angles. The H-atom abstraction channel to form OH was also observed. The OH product was mostly forward-scattered with relatively small loss of translational energy, indicative of a stripping mechanism. An H-atom elimination mechanism to form the ethoxy radical was observed for the first time. The ethoxy product was found to be scattered forward, sideways, and backwards with dips in the angular distribution, and the translational energy distribution was found to be peaked at low energy, implying large energy transfer into the formed ethoxy product. The excitation function of the H-atom elimination reaction was also measured and compared to theoretical calculations. The upper limit to the reaction barrier of this channel was found to be  $\sim 60$  kcal mol<sup>-1</sup>. The final channel studied was the C–C bond breakage channel, which was seen experimentally for the first time. The  $OCH_3$  product was found to be mostly forward scattered with an average of  $\sim 60\%$  of the translational energy going into internal energy of the  $OCH_3$  and  $CH_3$  products. The following relative product yields were obtained for all of the observed channels: 85% for O atom inelastic scattering, 10% for H-atom abstraction, 4% for H-atom elimination, and 1% for C–C bond breakage.

### **Hyperthermal atom scattering dynamics from surfaces**

#### *Synergistic effects on FEP Teflon involving O atoms, Ar atoms, and VUV light*

Atomic oxygen and molecular nitrogen at low Earth orbital (LEO) altitudes collide with spacecraft surfaces at relative velocities of  $\sim 7.4$  km s<sup>-1</sup>. The energy associated with these hyperthermal collisions may help promote materials degradation through collision-induced dissociation (CID) or reaction. Spacecraft are also exposed to high fluxes of vacuum ultraviolet (VUV) radiation, which may degrade materials through various photochemical mechanisms. We have investigated the roles of atomic oxygen, VUV light, and CID in the degradation of FEP Teflon by conducting beam-surface scattering experiments that probed products scattered from an FEP Teflon surface that was bombarded by various combinations of  $O(^3P)$  atoms, Ar atoms, and VUV light. A laser-detonation source was used to create hyperthermal beams of atomic oxygen and argon. A filtered deuterium lamp provided a source of VUV light. FEP Teflon that was exposed to VUV light alone yielded volatile reaction products. O atoms with 5 eV of translational energy did not react with a pristine surface, but reaction products were observed when VUV light also bombarded the surface. Scattered products were detected when Ar atoms, with translational energies greater than  $\sim 8$  eV, were directed at a pristine surface, indicating that energetic collisions alone may lead to bond breakage and mass loss at an FEP Teflon surface.



Thus, both energetic collisions and VUV light may produce radical sites where O atoms can react. The scattered CID product signal increased significantly when VUV light was present, suggesting that VUV light plays an important synergistic role in the mass loss of FEP Teflon not only by creating reactive sites but also by producing relatively light fragments that can be dislodged from the surface by energetic gas-surface collisions.

#### Energy transfer in hyperthermal collisions of Ar with graphite

Experiments and simulations for the scattering of hyperthermal Ar atoms from an ordered HOPG surface were conducted in collaboration with Steven Sibener (U. of Chicago) and Diego Troya (Virginia Tech). For all of the incident angles, incident energies (2.8-14.1 eV), and surface temperatures (150-700 K), the in-plane scattered flux was concentrated into narrow superspecular features with significant energy loss. The simulations did a good job of duplicating these results. Of particular interest was the comparison with hyperthermal Xe scattering from the same surface. For the entire range of Xe energies (0.5-3.6 eV), the scattering can be reproduced using a simple hard cubes model with a surface mass of ~300 amu. For Ar, the energy exchange with the surface is much larger than predicted by a hard cubes model. Overall, the angular dependence of the energy appears to be in the structure scattering regime, where the interaction is with only one or a few surface atoms. In fact, a simple binary model, derived using the assumption of a single collision between two spheres, does approximately represent the data. However, this requires a surface mass of 70-100 amu, and is physically unreasonable in that the simulation shows that there are multiple collisions with more than one surface atom. Some of the simulations were performed for the Xe scattering. It turns out that part of the apparently good agreement with the hard cubes model is due to the attractive part of the potential, something that the hard cubes model ignores. Though simple models are enticing, they sometimes actually obscure the physics.

### **Probing the effects of hyperthermal atomic oxygen on materials**

#### In situ monitoring of mass loss from polymers

In support of our studies to understand better how hyperthermal O atoms react with various polymers, both coated and uncoated, we purchased a quartz crystal microbalance (QCM), which provides the capability to measure in real time the mass loss of a polymer that is exposed to atomic oxygen. Our earlier studies only allowed for post-exposure characterization of exposed materials, making kinetic studies of erosion extremely difficult. With the QCM, we can study these kinetics fairly easily. Part of the technology that had to be developed to use the QCM was learning how to prepare coat the QCM discs with polyimide films. We learned how to coat the QCM crystals with a pure (control) polyimide, and tested the utility of the QCM to measure *in situ* the mass loss of this control polymer during O-atom attack. We went on to use the QCM to measure mass-loss rates for a variety of POSS-containing polyimides and for pure polyimides that were coated with alumina.

A novel coating method – atomic layer deposition (ALD) – can produce higher quality oxide coatings that are very thin and have no defects. These coatings have not yet been employed in space, because their efficacy for protecting polymers has not been tested. Another approach to the production of space-survivable polyimides is to incorporate polyhedral oligomeric silsesquioxanes (POSS) into the polyimide structure, thereby creating an



inorganic/organic hybrid polymer. Earlier studies indicate that the POSS polyimides form a passivating  $\text{SiO}_2$  layer which resists atomic oxygen attack.  $\text{Al}_2\text{O}_3$  coatings were applied to polyimide surfaces by ALD in the lab of Steven George at CU Boulder, and these coated samples were exposed to the atomic-oxygen beam in the PI's lab. The threshold thickness for protection was determined to be 3.5 nm. We studied the erosion kinetics of POSS-containing polyimide films prepared with starting materials supplied by Sandra Tomczak from AFRL/Edwards AFB. In order to evaluate the erosion kinetics of POSS polyimides, we proposed a kinetic model and successfully used it to fit data on the erosion depth of POSS polyimide materials as a function of atomic-oxygen fluence. For POSS polyimides, the mass loss rate is initially large but quickly decreases and tends toward a small terminal value, consistent with the formation of a passivating layer on the surface. The quantitative erosion rate (and therefore the values of model parameters) depends on the formulation of the POSS polyimide.

#### Simulated space environmental effects

Many samples were exposed to the hyperthermal atomic-oxygen beam, and *ex situ* analyses were conducted on the samples. The analyses by personnel in the PI's group included recession measurements with a profilometer, surface chemistry analysis by XPS, and surface topographical analysis by AFM and SEM. Some samples were sent to the sample providers for further analyses beyond the capabilities of the PI.

The structure of the oxide and interface formed on Si(100) at 493 K by 5.1 eV hyperthermal atomic oxygen and thermal molecular oxygen were studied in collaboration with Prof. Judith Yang from the University of Pittsburgh. We found that the ability for hyperthermal atomic oxygen to attack equally the uppermost, first, and second backbond layers in silicon could explain the initial increased linear oxide kinetics, homogeneity of the oxide, and interface abruptness with minimal presence of suboxides near the interface. The continual production of available electrons due to thermionic emission, facilitated by the 5.1 eV of O-atom kinetic energy may enhance the oxidation rate of Si(100), leading to enhanced growth and thicker oxide as compared to the growth kinetics for molecular oxygen which passivate within a few monolayers of oxide. The energy of the atomic oxygen could also cause a limited ordering of the amorphous silica towards its thermodynamically stable phase, alpha-quartz.

A series of four new end-capped and hydroxymethyl-functionalized polyimides were prepared by Sandra Tomczak (AFRL) and coworkers, and the durability of these polymers against atomic-oxygen attack was investigated in the PI's lab. Through a two-step chemical modification process (3-aminopropyl)(hepta-*i*-butyl) polyhedral oligomeric silsesquioxane (POSS) was covalently attached to the polymer backbone. POSS loading levels as high as 36 wt % could be obtained while maintaining excellent processability and optical clarity of thin films. Concurrent attachment of either a cyanate ester or hydroxyethyl methacrylate (HEMA) group afforded processable POSS polyimides that underwent thermal curing to yield solvent-resistant films, both having final  $T_g$ 's of 251 °C. Kinetic analysis of the cure reactions yielded energy of activations of 93 kJ/mol (cyanate ester) and 103 kJ/mol (HEMA). Exposure of a POSS-polyimide containing ~31 wt % POSS to atomic oxygen displayed no measurable level of erosion relative to a Kapton H standard.

Although erosion mechanisms of polymers by hyperthermal atomic oxygen in low Earth orbit are not well understood, an empirical model has been developed by Iskanderova et al. which suggests that the erosion yield of a hydrocarbon-based polymer is proportional to the



quantity,  $N_T / N_C^*$ , where  $N_T$  is the total number of atoms in a polymer repeat unit and  $N_C^*$  is the number of "effective" carbon atoms in the polymer repeat unit that must react with attacking O atoms so that erosion can proceed. In order to test this model and to probe the chemistry that governs hydrocarbon polymer erosion by hyperthermal oxygen atoms, we investigated the erosion yields of polymers containing several different functional groups. In particular, we performed careful measurements of the erosion yields of poly(ethylene), poly(propylene), polyvinyl alcohol, poly(ethylene oxide), poly(vinyl chloride), poly(vinyl methyl ketone), poly(vinyl acetate), and poly(acrylic acid) when these materials were exposed to a beam of 5 eV oxygen atoms produced by a laser-detonation source. We found that the erosion yields of these materials were not predicted quantitatively by the empirical model. The relative erosion yield of each polymer might thus be dependent on rate-limiting processes other than formation of CO and CO<sub>2</sub> (the basic assumption of the model). Such a rate limiting process might only apply to a temperature-dependent mechanism which occurs concomitantly with a temperature-independent mechanism. A candidate rate-limiting reaction is H-atom abstraction. Our results suggest that a quantitative model of the erosion yield of a polymer should consider the chemical environments of the atoms which may be involved in rate-limiting reactions with atomic oxygen.

## PERSONNEL SUPPORTED

### Year 1 (7/1/04 - 6/30/05)

- a) Timothy K. Minton, Montana State University PI (20%)
- b) Jianming Zhang, senior research staff member (100%)
- c) Hari Upadhyaya, post-doc (20%)
- d) Niki Megaard, lab assistant (33%)

### Year 2 (7/1/05 - 6/30/06)

- a) Timothy K. Minton, Montana State University PI (7%)
- b) Jianming Zhang, senior research staff member (33%)
- c) Hari Upadhyaya, post-doc (17%)
- d) Evgueni Kadossov, post-doc (8%)
- e) Amy Brunsvold, graduate student (33%)
- f) Amelia Valasek, graduate student (25%)
- g) Russell Cooper, undergraduate student (33%)

### Year 3 (7/1/06 - 6/30/07)

- a) David Stockdale, undergraduate student (17%)
- b) Russell Cooper, undergraduate student (8%)

## PUBLICATIONS

### Student Thesis

1. "Molecular Beam Studies of Hyperthermal Atomic Oxygen and Argon Interactions with Polymer Surfaces and Gas-Phase Molecules," Amy L. Brunsvold, Ph.D. Thesis, May 2007.



### Journal Articles

1. "Experimental and Theoretical Investigations of the Inelastic and Reactive Scattering Dynamics of  $O(^3P) + D_2$ ," D. J. Garton, A. L. Brunsvold, T. K. Minton, D. Troya, B. Maiti, and G. C. Schatz, *J. Phys. Chem. A* **110**, 1327-1341 (2006).
2. "Erosion of Kapton H by Hyperthermal Atomic Oxygen," D. M. Buczala, A. L. Brunsvold, and T. K. Minton, *J. Spacecraft and Rockets* **43**, 421-425 (2006).
3. "Chemical Modification of Fluorinated Polyimides: New Thermally Curing Hybrid Polymers with POSS," Michael E. Wright, Brian J. Petteys, Andrew J. Gruenthner, Stephen Fallis, Gregory R. Yandek, Sandra J. Tomczak, Timothy K. Minton, and Amy L. Brunsvold, *Macromolecules* **39**, 4710-4718 (2006).
4. "Hyperthermal Reactions of O and  $O_2$  with a Hydrocarbon Surface: Direct C-C Bond Breakage by O and H-Atom Abstraction by  $O_2$ ," Jianming Zhang, Hari P. Upadhyaya, Amy L. Brunsvold, and Timothy K. Minton, *J. Phys. Chem. B* **110**, 12500-12511 (2006).
5. "Protection of a Polymer from Atomic-Oxygen Attack by Thin Coatings of  $Al_2O_3$  Prepared by Atomic Layer Deposition," R. Cooper, H. P. Upadhyaya, T. K. Minton, X. Du, S. M. George, and M. R. Berman, *Thin Solid Films*, doi:10.1016/j.tsf.2007.07.150, in press, posted online September 20, 2007.
6. "Crossed-Beams and Theoretical Studies of the  $O(^3P) + H_2O \rightarrow HO_2 + H$  Reaction Excitation Function," A. L. Brunsvold, J. Zhang, H. P. Upadhyaya, T. K. Minton, J. P. Camden, J. T. Paci, and G. C. Schatz, *J. Phys. Chem. A* **111**, 10907-10913 (2007).
7. "A Crossed Molecular Beams Study of Hyperthermal Interactions of  $O(^3P)$  and CO," A. L. Brunsvold, H. P. Upadhyaya, J. Zhang, R. Cooper, T. K. Minton, and M. Braunstein, *J. Phys. Chem. A*, accepted for publication, December 28, 2007.

### Draft manuscripts written – to be submitted in 2008

1. "Inelastic and Reactive Scattering Dynamics of  $O(^3P)$  Collisions with  $C_2H_6$ ," D. J. Garton, T. K. Minton, W.-F. Du, and G. C. Schatz, to be submitted to *J. Phys. Chem. A*.
2. "Beam-Surface Scattering Studies of the Individual and Combined Effects of VUV Radiation and Hyperthermal O,  $O_2$ , or Ar Atoms on FEP Teflon Surfaces," Amy L. Brunsvold, Hari P. Upadhyaya, Jianming Zhang, and Timothy K. Minton, to be submitted to *Applied Surface Science*.
3. "Crossed-Beams and Theoretical Studies of Hyperthermal Reactions of  $O(^3P)$  with HCl," J. Zhang, A. L. Brunsvold, H. P. Upadhyaya, T. K. Minton, S. Garashchuk, J. P. Camden, J. T. Paci, and G. C. Schatz, to be submitted to *J. Phys. Chem. A*.
4. "Hyperthermal Ar-Atom Scattering from a C(0001) Surface," K. D. Gibson, S. J. Sibener, H. P. Upadhyaya, A. L. Brunsvold, J. Zhang, T. K. Minton, and D. Troya, to be submitted to *J. Phys. Chem. C*.



### Conference Proceedings

1. "Increased Ordering in Amorphous SiO<sub>x</sub> due to Hyperthermal Atomic Oxygen," M. Kisa, W. G. Stratton, T. K. Minton, K. Van Benthem, S. J. Pennycook, P. M. Voyles, X. Chen, L. Li, and J. C. Yang, in *Proceedings of the 2004 Fall Meeting of the Materials Research Society -- Volume 851*, Edited by M. Chipara, D. L. Edwards, S. Phillips, and R. Benson.
2. "Properties and Improved Space Survivability of POSS (Polyhedral Oligomeric Silsesquioxane) Polyimides", Sandra J. Tomczak, Darrell Marchant, Steve Svejda, Timothy K. Minton, Amy L. Brunsvold, Irina Gouzman, Eitan Grossman, George C. Schatz, Diego Troya, Li-Peng Sun, and Rene I. Gonzalez, in *Proceedings of the 2004 Fall Meeting of the Materials Research Society -- Volume 851*, Edited by M. Chipara, D. L. Edwards, S. Phillips, and R. Benson.
3. "Beam-Surface Scattering Studies of the Individual and Combined Interactions of VUV Radiation and Hyperthermal O, O<sub>2</sub>, or Ar with Fluorocarbon Surfaces," A. L. Brunsvold, H. P. Upadhyaya, J. Zhang, and T. K. Minton, in *Proceedings of the 10<sup>th</sup> International Symposium on Materials in a Space Environment*, Collioure, France, June 19-23, 2006.
4. "Probing the Effects of Molecular Structure on the Erosion of Hydrocarbon-Based Polymers by Atomic Oxygen," D. J. Minton, D. P. Stockdale, D.-C. Lee, L. Yu, and T. K. Minton, in *Proceedings of the 10<sup>th</sup> International Symposium on Materials in a Space Environment*, Collioure, France, June 19-23, 2006.
5. "Polyhedral Oligomeric Silsesquioxane (POSS) Polyimides as Space-Survivable Materials," S. J. Tomczak, V. Vij, D. Marchant, T. K. Minton, A. L. Brunsvold, M. E. Wright, B. J. Pettys, A. J. Guenther, G. R. Yandek, and J. Mabry, in *Proceedings of the SPIE Optics and Photonics Conference*, held in San Diego, CA, August 13-17, 2006.
6. "Comparisons of Polyhedral Oligomeric Silsesquioxane Polyimides as Space-Survivable Materials" Sandra J. Tomczak, Vandana Vij, Timothy K. Minton, Amy Brunsvold, Darrell Marchant, Michael E. Wright, Brian J. Petteys, Andrew J. Guenther, Gregory R. Yandek and Joseph M. Mabry, in *Polymer Durability and Radiation Effects*, Mathew C. Celina and Roger A. Assink, Eds.; ACS Symposium Series, American Chemical Society, Washington, DC, 2008, 978, 140-152.

### INTERACTIONS/TRANSITIONS

#### Participation/presentations at meetings, conferences, seminars, etc.

##### Invited talks

1. "Hyperthermal Reactions of O(<sup>3</sup>P) with Hydrogen and Methane," Dalian Institute of Chemical Physics Symposium on Molecular Dynamics (IV), Dalian, China, July 21-23, 2004.



2. "Reaction Dynamics Relevant to Spacecraft in Low-Earth Orbit: Atomic Oxygen Reactions with Gaseous and Surface Hydrocarbons," University of Hawaii, Manoa, October 11, 2004.
3. "Reaction Dynamics Relevant to Spacecraft and Missiles: Hyperthermal Atomic Oxygen Reactions," Montana State University, October 22, 2004.
4. "Reaction Dynamics Relevant to Spacecraft in Low-Earth Orbit: Atomic-Oxygen Reactions with Gaseous and Surface Hydrocarbons," University of California – Davis, November 16, 2004.
5. "Hyperthermal Reactions of  $O(^3P)$  with Hydrogen and Methane," *Gordon Research Conference on Molecular Energy Transfer*, Buellton, California, January 9-14, 2005.
6. "Atomic Beam-Surface Scattering Studies of the Combined Effects of VUV Radiation and Hyperthermal O,  $O_2$ , and Ar Atoms on the Erosion of FEP Teflon Surfaces," Amy L. Brunsvold, presented at the *Materials Research Society National Meeting*, San Francisco, CA, March 28 - April 1, 2005. (presented by student)
7. "Laboratory Studies of Hyperthermal O-Atom Reactions," *2005 Maui Analysis of Upper Atmosphere Injections (MAUI) Space Experiment Workshop*, Wailea, Maui, HI, September 5, 2005.
8. "Crossed-Beam and Beam-Surface Scattering Studies of Hyperthermal O and Ar Interactions," *International Symposium on Application of Quantum Beams 2005*, Kobe University, Kobe, Japan, October 18-19, 2005.
9. "Laboratory Studies of the Low-Earth-Orbital Environment," Amy L. Brunsvold, *Zonta International Montana Chapter Meeting, Keynote Speaker*, November 15, 2005. (presented by student)
10. "Hyperthermal Reactions of Oxygen Atoms with Spacecraft Materials and Rocket Plumes," Texas Tech University, Lubbock, TX, October 4, 2006.
11. "Crossed-Beams Studies of Hyperthermal  $O(^3P)$  Reactions," *Dalian Institute of Chemical Physics Symposium on Molecular Dynamics*, Dalian, China, October 18-21, 2006.
12. "Crossed-Beams Studies of Hyperthermal  $O(^3P)$  Reactions," *Trends in Chemical Dynamics: From Small Molecules to Biomolecules (an international symposium to honor Prof. Y. T. Lee on the occasion of his 70<sup>th</sup> birthday)*, Chiao Hsi, Yi-Lan County, Taiwan, December 10-15, 2006.
13. "Crossed-Beams Studies of Hyperthermal  $O(^3P)$  Reactions," *AFOSR Molecular Dynamics Contractors' Meeting*, Irvine, CA May 20-22, 2007.

#### Contributed talks

1. "Atomic Beam-Surface Scattering Studies of the Individual and Combined Effects of VUV Radiation and Hyperthermal O or Ar Atoms on FEP Teflon Surfaces," *International Chemical Conference of Pacific Basin Societies (Pacifichem) 2005*, Honolulu, HI, Dec. 19, 2005.
2. "Beam-Surface Scattering Studies of the Individual and Combined Interactions of VUV Radiation and Hyperthermal O,  $O_2$ , or Ar with Fluorocarbon Surfaces," *10<sup>th</sup> International Symposium on Materials in a Space Environment*, Collioure, France, June 19-23, 2006.



3. "A Crossed Molecular Beams Study of the Hyperthermal Interactions of  $O(^3P)$  and CO," Amy L. Brunsvold, 232<sup>nd</sup> *American Chemical Society National Meeting*, San Francisco, CA, September 10 - 14, 2006. (presented by student)
4. "Atomic Beam-Surface Scattering Studies of Hyperthermal Ar or O Atoms on Graphite Surfaces," Hari P. Upadhyaya, 232<sup>nd</sup> *American Chemical Society National Meeting*, San Francisco, CA, September 10 - 14, 2006. (presented by post-doc)
5. "Hyperthermal Reactions of O and O<sub>2</sub> with a Hydrocarbon Surface: Direct C-C Bond Breakage by O and H-Atom Abstraction by O<sub>2</sub>," Jianming Zhang, Hari P. Upadhyaya, Amy L. Brunsvold, and Timothy K. Minton, 232<sup>nd</sup> *American Chemical Society National Meeting*, San Francisco, CA, September 10 - 14, 2006. (presented by senior research staff member)
6. "Beam-Surface Scattering Studies of the Individual and Combined Effects of VUV Radiation and Hyperthermal O, O<sub>2</sub>, or Ar Atoms on FEP Teflon Surfaces," Amy L. Brunsvold, *Montana ACS Meeting in Miniature*, Carroll College, Helena, MT, April 1, 2006. (presented by student)
7. "Beam-Surface Scattering Studies of the Individual and Combined Effects of VUV Radiation and Hyperthermal O, O<sub>2</sub>, or Ar Atoms on FEP Teflon Surfaces," Amy L. Brunsvold, *National Space and Missile Materials Symposium*, Orlando, FL, June 24-30, 2006. (presented by student)

#### Posters

1. "Beam-Surface and Crossed-Beams Studies of Hyperthermal  $O(^3P)$  Reactions with Saturated Hydrocarbons," D. J. Garton, J. Zhang, T. K. Minton, D. Troya, and G. C. Schatz, *Gordon Research Conference on Molecular Energy Transfer*, Buellton, CA, January 11-14, 2005. (presented by former student)
2. "Energy Transfer in Hyperthermal Collisions of Ar with Ethane," A. L. Brunsvold, D. J. Garton, T. K. Minton, D. Troya, and G. C. Schatz, *Gordon Research Conference on Molecular Energy Transfer*, Buellton, CA, January 11-14, 2005. (presented by student)
3. "Collision-Induced Desorption of Chlorine from a Chlorinated Silicon Surface," J. Zhang and T. K. Minton, *Gordon Research Conference on Molecular Energy Transfer*, Buellton, CA, 11-14 January 11-14, 2005. (presented by senior research staff member)
4. "Atomic Beam-Surface Scattering Studies of the Individual and Combined Effects of VUV Radiation and Hyperthermal O, O<sub>2</sub>, or Ar on the Erosion of FEP Teflon Surfaces," A. L. Brunsvold, H. P. Upadhyaya, J. Zhang, and T. K. Minton, *AFOSR MURI Program Review*, Bozeman, MT, January 27-28, 2005. (presented by student)
5. "An Investigation of the Resistance of POSS Polyimide to Atomic-Oxygen Attack," A. L. Brunsvold, T. K. Minton, I. Gouzman, Eitan Grossman, S. J. Tomczak, and R. I. Gonzalez, *AFOSR MURI Program Review*, Bozeman, MT, January 27-28, 2005. (presented by student)



6. "Energy Transfer in Hyperthermal Collisions of Ar with Ethane," A. L. Brunsvold, D. J. Garton, T. K. Minton, and G. C. Schatz, *AFOSR MURI Program Review*, Bozeman, MT, January 27-28, 2005. (presented by student)
7. "Reaction Dynamics Relevant to Spacecraft in Low-Earth Orbit: Atomic-Oxygen Reactions with Gaseous and Surface Hydrocarbons," T. K. Minton, D. J. Garton, J. Zhang, A. Brunsvold, D. Troya, B. Maiti, and G. C. Schatz, *2005 AFOSR Molecular Dynamics Contractors' Meeting*, Monterrey, CA, May 22-24, 2005.
8. "Beam-Surface Scattering Studies of the Individual and Combined Effects of VUV Radiation and Hyperthermal O, O<sub>2</sub>, or Ar with Fluorocarbon Surfaces," A. L. Brunsvold, H. P. Upadhyaya, J. Zhang, and T. K. Minton, *XXth Conference on the Dynamics of Molecular Collisions*, Pacific Grove, CA, July 10-15, 2005. (presented by student)
9. "Hyperthermal O(<sup>3</sup>P) Reactions with a Saturated Hydrocarbon Surface," J. Zhang, D. J. Garton, T. K. Minton, D. Troya, and G. C. Schatz, *XXth Conference on the Dynamics of Molecular Collisions*, Pacific Grove, CA, July 10-15, 2005. (presented by senior research staff member)
10. "Beam-Surface Scattering Studies of the individual and Combined Interactions of VUV Radiation and Hyperthermal O, O<sub>2</sub>, or Ar with Fluorocarbon Surfaces," A. L. Brunsvold, H. P. Upadhyaya, J. Zhang, and T. K. Minton, *Gordon Research Conference on Dynamics at Surfaces*, Andover, NH, August 14-19, 2005. (presented by student)
11. "Hyperthermal Reactions of O and O<sub>2</sub> with a Hydrocarbon Surface: Direct C-C Bond Breakage by O and H-Atom Abstraction by O<sub>2</sub>," J. Zhang, H. P. Upadhyaya, A. L. Brunsvold, and T. K. Minton, *2006 AFOSR Molecular Dynamics Contractors' Meeting*, Arlington, VA, June 5-7, 2006.
12. "Effect of Polymer Structure on the Erosion of Hydrocarbon-Based Polymers by Atomic Oxygen," D. J. Garton, D. P. Stockdale, D.-C. Lee, L. Yu, and T. K. Minton, *10<sup>th</sup> International Symposium on Materials in a Space Environment*, Collioure, France, June 19-23, 2006. (presented by former student)
13. "Effect of Polymer Structure on the Erosion of Hydrocarbon-Based Polymers by Atomic Oxygen," D. J. Garton, D. P. Stockdale, D.-C. Lee, L. Yu, and T. K. Minton, *2006 National Space & Missile Materials Symposium*, Orlando, FL, June 24-30, 2006. (presented by student)
14. "Erosion Kinetics of Polyimides Exposed to Atomic Oxygen," R. Cooper, H. P. Upadhyaya, A. L. Brunsvold, J. Zhang, T. K. Minton, and S. J. Tomczak, *2006 National Space & Missile Materials Symposium*, Orlando, FL, June 24-30, 2006. (presented by student)
15. "Surface Modification of Novel Metal-Containing Polymers by Hyperthermal Atomic Oxygen," T. Horne, D. J. Garton, L. Yu, and T. K. Minton, *2006 National Space & Missile Materials Symposium*, Orlando, FL, June 24-30, 2006. (presented by student)



16. "Crossed-Beams and Beam-Surface Scattering Studies of Hyperthermal  $O(^3P)$  Reactions," D. J. Garton, J. Zhang, A. L. Brunsvold, H. P. Upadhyaya, T. K. Minton, W.-F. Du, G. C. Schatz, and D. Troya, *Trends in Chemical Dynamics: From Small Molecules to Biomolecules*, Chiao Hsi, Yi-Lan County, Taiwan, December 10-15, 2006.

17. "Crossed-Beams and Theoretical Studies of Hyperthermal Reactions of  $O(^3P)$  with HCl and  $H_2O$ ," J. Zhang, A. L. Brunsvold, H. P. Upadhyaya, T. K. Minton, J. P. Camden, J. T. Paci, and G. C. Schatz, *XXIst Conference on the Dynamics of Molecular Collisions*, Santa Fe, NM, July 8-13, 2007. (presented by senior research staff member)

### **Consultative and advisory functions**

Senior Editor of Journal of Physical Chemistry A/B/C. The PI facilitates the peer-review process and makes decisions on ~450 manuscripts per year. May 1, 2005 to present.

#### Conference organization by PI.

(1) Organizer of symposium ("Chemical Dynamics in Extreme Environments") held at the ACS National Meeting, San Francisco, September 10-14, 2006.

(2) Co-Organizer of symposium ("In Situ Studies of Gas-Solid Surface Reactions") held at the Materials Research Society National Meeting in San Francisco, CA, Mar. 28 - Apr. 1, 2005.

MURI Center for Materials Chemistry in the Space Environment. The work supported by AFOSR on this grant has used scientific and financial leverage from an AFOSR-funded MURI center whose focus is on materials degradation in the space environment. The PI is a member of this MURI center that also includes the following people:

Prof. Steven Sibener, University of Chicago (collaborator on HOPG work)

Prof. Luping Yu, University of Chicago

Prof. Dennis Jacobs, Notre Dame University

Prof. George Schatz, Northwestern University (collaborator on  $O + H_2$ /alkane work)

Prof. John Tully, Yale University

Prof. Barbara Garrison, Penn State University

Prof. Bill Hase, Wayne State University

Dr. Sandra Tomczak, AFRL, Edwards AFB. Dr. Tomczak provided samples of POSS polymers to our lab, and we investigated the resistance of these polymers to atomic oxygen attack.

Prof. Judy Yang, University of Pittsburgh. The PI has conducted sample exposures of semiconductors and metals for Prof. Yang, and she has done analysis with variety of surface analytical techniques, mostly centered around electron microscopy.

Dr. Matt Braunstein, Spectral Sciences, Inc. Dr. Braunstein is an expert on modeling rocket plume phenomenology. Experiments have been conducted in the PI's lab that help validate the direct simulation Monte Carlo (DSMC) code that has been developed by Dr. Braunstein and his colleagues. Furthermore, Dr. Braunstein has collaborated with the PI by conducting theoretical calculations that relate to the PI's experiments on  $O + CO$ .



Dr. Rainer Dressler, AFRL, Hanscom AFB. The PI was invited to participate in a meeting organized by Dr. Dressler on the Maui Analysis of Upper-Atmosphere Injections. The work being conducted by the PI is providing input for understanding the chemistry that occurs in rocket plumes in the upper atmosphere.

Dr. Jacob Kleiman, Integrity Testing Laboratory, Toronto, Canada. Dr. Kleiman owns a small company that does many types of materials testing. Dr. Kleiman and the PI have had many informal discussions about O-atom sources and about the best way to simulate space environmental effects.

Dr. Gary Pippin, Boeing Phantom Works, Seattle. Dr. Pippin has organized many space flight experiments and is currently involved in several MISSE (Materials International Space Station Experiment) experiments. The PI has provided polymer samples to Dr. Pippin for future experiments and is also helping him plan for additional flight experiments.

## **Transitions**

Dr. Sandra Tomczak (AFRL, Edwards AFB). Dr. Tomczak has been the manager of a project for DARPA to investigate the use of POSS polyimides as space-survivable, multifunctional materials in low Earth orbit. The PI has applied the infrastructure generated from the DEPSCoR project to the O-atom testing on new POSS polyimides that were developed as part of this program. Many new POSS materials were prepared and found to be resistant to atomic-oxygen attack in the PI's lab.

Center for Laboratory Studies of Rocket Plume Chemistry. The work done in the PI's lab, largely as part of this grant and a prior DEPSCoR grant, has attracted the attention of various researchers who are working on rocket plume chemistry relevant to missile defense. Following many discussions with members of this community, the PI submitted a proposal to Senator Conrad Burns (Montana), who obtained a Congressional appropriation that enabled the PI to establish a center at Montana State University for the study of rocket plume chemistry. The Center is now very productive, after receiving funding from two appropriations. This Center has enhanced research infrastructure at Montana State University and should lead to experimental data that will aid in modeling efforts for the Missile Defense Agency and for the Air Force. Already, new data have been used by Spectral Sciences, Inc. to improve their SOCRATES plume modeling code.

ALD NanoSolutions, Broomfield, CO and Alameda Applied Sciences Corporation, San Leandro, CA. A collaborative project was conducted with Steven George (CU Boulder) on the efficacy of  $\text{Al}_2\text{O}_3$  atomic layer deposition coatings to protect polymers from atomic-oxygen attack. This work showed that  $\text{Al}_2\text{O}_3$  coatings of ~3.5 nm thickness are sufficient to protect the underlying substrate. Based on the success of this work, the PI has become involved in STTR projects ALD NanoSolutions and Alameda Applied Sciences Corporation on the protection of polymers from atomic oxygen, VUV light, and static charge buildup with the use of novel coatings. Both companies are actively developing coatings that are being tested in the PI's lab. The hope is that one or both of these approaches will lead to commercially viable coatings that will improve



materials durability in space. A commercial partner, Boeing, is interested in the outcome of the new research.

#### **NEW DISCOVERIES, INVENTIONS, OR PATENT DISCLOSURES**

NONE

#### **HONORS/AWARDS**

##### **a) awards/honors received during grant period**

Visiting Associate Professor at the James Franck Institute,  
University of Chicago, Summer 2004 (T. K. Minton)

Amelia Earhart Fellowship, 2005-2006; renewed 2006-2007 (Amy L. Brunsvold, grad. student)

Montana Space Grant Fellowship, 2006-2007 (Amy L. Brunsvold, grad. student)

##### **b) lifetime achievement honors (T. K. Minton)**

Aurora Illinois Foundation Undergraduate Scholarship, 1976-80

University of Illinois Summer Fellowship, 1979

NASA Award for a Technological Contribution, 1995

MSU Alumni/Bozeman Chamber of Commerce Excellence Award, 1996

Charles and Nora L. Wiley Faculty Award for Meritorious Research, May 2002

Air Force Research Laboratory, In-House Project of the Quarter: "Space-Survivable Polymers  
Containing Polyhedral Oligomeric Silsesquioxanes (POSS)", Fall 2002

Visiting Associate Professor at the James Franck Institute, University of Chicago, Summer 2004